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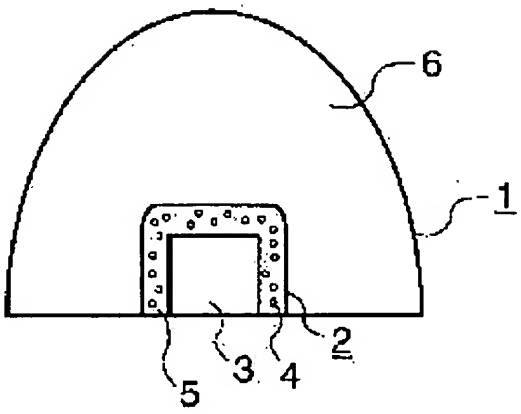
(54) LIGHT EMITTING ELEMENT

(57)Abstract:

PROBLEM TO BE SOLVED: To improve the lifetime of a light emitting element.

SOLUTION: The light emitting element 1 is provided with a light emitting diode 3 and a fluorescence layer 2. In order to improve the lifetime of the light emitting element 1, fluorescent substance 4 of the fluorescence layer 2 is provided with water-resistant coating.



DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the light emitting device which prepared at least one light emitting diode and a fluorescence layer.
[0002]
[Description of the Prior Art] The solid-state light source, for example, light emitting diode, especially semiconductor diode are known conventionally. Luminescence of semiconductor diode is based on the recombination of an electronic-hole pair (exciton) of the transition region of pn transition of the semi-conductor which was able to apply bias to the forward direction. The dimension of the band gap of a semi-conductor determines the wavelength of the emitted light roughly.
[0003] The semiconductor diode which emits the light is used also with a color display. In a color display, red, green, and blue in three primary colors are generated by the array of red luminescence semiconductor diode, green luminescence semiconductor diode, and blue luminescence semiconductor diode. However, the approach of attaining the color picture description near a genuine article, especially true description green [in an image] and blue in this case poses a problem.
[0004] By development of the semiconductor diode which performs UV radiation, the possibility of the true color picture display on the color picture screen which addresses diode is increasing. By combining the semiconductor diode which performs UV radiation, and the emitter which changes UV radiation into the light, the color and white of the arbitration of the lights of the request by semiconductor diode can be expressed. Such a color display is known from the Germany patent number No. 19800983. This principle is applied also to the semiconductor diode which carries out outgoing radiation of purple or the blue glow, when using a suitable emitter.
[0005]
[Problem(s) to be Solved by the Invention] The main advantages of the luminescence semiconductor diode at the time of comparing with the conventional lamp are the long lives accompanying high stability and high it. The limiting factor of the color picture screen which addresses diode is the stability of the fluorescent substance used in a fluorescence layer. Since a fluorescent substance is not thoroughly separated from a circumference ambient atmosphere, the fluorescent substance reacted to water has a possibility that the moisture from air may hydrolyze. A comparatively stable fluorescent substance also has a possibility of hydrolyzing under an elevated temperature and the effect of high humidity. The life of a light emitting device is shortened by degradation of the fluorescent substance in a fluorescence layer.
[0006] The object of this invention is offering the light emitting device whose life in which light emitting diode and a fluorescence layer were prepared improved.
[0007]
[Means for Solving the Problem] This object prepares at least one light emitting diode and a fluorescence layer, and it is attained by the light emitting device to which this fluorescent substance is characterized by having at least one fluorescent substance which has coating.
[0008] Degradation produced with the moisture in air is prevented by coating of the fluorescent substance particle which has the waterproof film of high density.
[0009] Suitably, said coating is chosen from the group which consists of an organic material, an inorganic material, and a glass ingredient.
[0010] Furthermore, said organic material is suitably chosen from the group which consists of a latex and polyorganosiloxane.
[0011] Furthermore, said glass ingredient is suitably chosen from the group which consists of a borosilicate, a phospho silicate, and an alkali silicate.
[0012] Furthermore, said inorganic material is suitably chosen from the group which consists of combination of an oxide, a borate, phosphate, and these ingredients.
[0013] It does not deteriorate by radiation which these organic materials, a glass ingredient, and an inorganic material form insoluble coating to water to a fluorescent substance particle by closing in, and the coating does not react with a fluorescent substance, and has the wavelength of UV radiation, i.e., 410 to 450 nm. Furthermore, coating is colorlessness, therefore does not affect the value of the color of a fluorescent substance.

[0014] A suitable example is characterized by considering as the orthophosphate MPO4 which chose said phosphate from the group which consists M of aluminum, La, Sc, Y, and Lu, or the polyphosphate which has the presentation (M0.5PO3) which chose the chain length n and M between 101 and 106 from calcium, Sr, and Ba.

[0015] These phosphate forms the fully bolted thin film which has the front face of high density on a fluorescent substance.

[0016] Suitably, said illuminant is chosen from the group which consists of an oxidization illuminant, a sulfuration illuminant, an ulmin acid illuminant, a boric-acid illuminant, a vanadium illuminant, and a silicic-acid illuminant.

[0017] By combining these emitters with a suitable activator, UV radiation or blue glow is further changed into the light of long wave length.

[0018] suitable -- said ulmin acid emitter -- Y3aluminum5O12:Ce, 3(Y, Gd) (aluminum, Ga)5O12:Ce, and BaMgAl10O17: -- it chooses from the group which consists of Eu and Mn.

[0019] If especially Y3aluminum 5O12 that has special coating is excited by blue glow, it will serve as a fluorescent substance which emits yellow.

[0020] Furthermore, said sulfuration emitter is suitably chosen from SrS:Eu, SrGa2 S4:Eu, 2 (aluminum (Sr, calcium, Ba), Ga) S4:Eu, SrY2 S4:Eu, S:Eu (Mg, calcium), SrS:Ce, CaS:Ce, CaLa2 S4:Ce and CaS:Ce, and the group that consists of Eu.

[0021] Especially the fluorescent substance containing a sulfide like SrS:Eu is hydrolyzed by the moisture in air based on the following reaction formulae.

A fluorescent substance is stabilized by SrS+2H2 O->Sr(OH)2+H2S, therefore coating which has a sulfide suitably.

[0022] Furthermore, said light emitting device contains suitably SrS:Eu which has coating of SiO2 and a silicate.

[0023]

[Embodiment of the Invention] As shown in drawing 1 , a light emitting device 1 is equipped with the diode 2 which emits UV radiation or blue glow when the easiest, and the fluorescence layer 2 prepared in diode 3. The fluorescence layer 2 is equipped with the clear layer 5 which has the fluorescent substance 4 which performed waterproof coating with the gestalt of this operation. The ingredient of a clear layer 5 can be used as polyacrylate (polyacrylate), polystyrol (polystyrol), an epoxy resin (epoxide resin), polypropylene, a polycarbonate, or some [other] polymers.

[0024] A light emitting device 1 like the product mass-produced is usually protected by the epoxy housing 6 with which the lens of an epoxy resin is fabricated. This lens plays the role which raises advice of the light from a light emitting device 1. With the gestalt of this operation, the fluorescence layer 2 may be formed between a clear layer 5 and the epoxy housing 6. The fluorescence layer 2 can also be formed as coating of the outside of the epoxy housing 6. The fluorescence layer 2 contains fluorescent substance mixture (phosphor) equipped with the fluorescent substance 4 which prepared coating in these cases. With the gestalt of other operations, the fluorescence layer 2 is formed from an epoxy resin, and coating is prepared in a fluorescent substance 4. With the gestalt of this operation, the fluorescence layer 2 forms the epoxy housing 6.

[0025] When a light emitting device should carry out outgoing radiation of the white light, a fluorescence layer includes physical mixing of the fluorescent substance which emits the fluorescent substance which emits red, the fluorescent substance which emits blue, and green.

[0026] A large-sized two-dimensional display can be easily manufactured by the array of light emitting diode 3. The array of such light emitting diode 3 can be covered with the glass plate against which it was pushed by the fluorescence layer 2. The fluorescence layer 2 is equipped with the red emitter, green emitter, and blue emitter which were prepared by the three-point pattern arranged to the triangle.

[0027] The diode 3 which carries out outgoing radiation of the UV contains INGaN or GaN. The diode 3 which carries out outgoing radiation of this UV has the maximum luminescence between 370nm which is half-value-width FWHM<50nm, and 410nm (emission maximun). The diode 3 which carries out outgoing radiation of the blue glow which has the wavelength between 410nm and 450nm has for example, InGaN/AlGaN structure. A means to supply electric energy to the diode 3 which carries out outgoing radiation of UV or the blue glow is established in order to maintain luminescence. The means has at least two electrodes.

[0028] Let the fluorescent substance used in the fluorescence layer 2 be for example, an oxidization fluorescent

substance, a sulfuration fluorescent substance, an ulmin acid fluorescent substance, a way acid fluorescent substance, a vanadium acid fluorescent substance, or a silicic acid fluorescent substance.
Especially :Y3aluminum5O12:Ce for which the following fluorescent substances are used, 3 (Y, Gd) 5O12: (aluminum, Ga) Ce, BaMgAl10O17: It Eu(s). Eu, Mn, Y2O2 S:Eu, Bi, and YVO4: -- Eu, Bi, and YVO4: -- Eu, Bi, and YBO3: -- Ce, Tb, 2(Sr, Ba) SiO4:Eu, calcium2MgSi2O7:Eu, Sr2CeO4:Eu, SrS:Eu, and SrGa2S4: -- (Sr, calcium, Ba) 2 S4:Eu, SrY2 S4:Eu, S:Eu (calcium, Sr), S:Eu (Mg, calcium), SrS:Ce, CaS:Ce, CaLa2 S4:Ce or CaS:Ce, Eu (aluminum, Ga).
[0029] The particle of a fluorescent substance 4 is covered in a flat waterproof layer by closing in. a logarithm -- the thickness of the layer of coating is usually 0.001 to 0.2 micrometer, therefore since it is dramatically thin, a photon can pass a layer, without losing most energy.
[0030] Formation of coating follows various approaches according to a coating ingredient.
[0031] In order to cover a fluorescent substance with a latex, a latex is dissolved with an organic solvent. Then, a fluorescent substance 4 suspends in this solvent (suspend). A latex precipitates to the particle of a fluorescent substance 2 by adding the solvent which a latex does not dissolve (precipitate). After filtering and drying the fluorescent substance by which coating was carried out, melting (fuse) of the latex is carried out at an elevated temperature.
[0032] Coating containing a polysiloxane is obtained by mixing a polysiloxane directly to a fluorescent substance 4. A polysiloxane can be fused to an organic solvent and this solvent can also be made to suspend a fluorescent substance 4 after that instead. Cross linking of the polysiloxane pasted up on the particle of a fluorescent substance 4 is carried out by overheating, the catalyst, or radical initiation (radicalinitiation) after evaporation of a solvent.
[0033] In order to manufacture glass type coating from a borosilicate, a phospho silicate (phosphosilicate), or an alkali silicate, the colloidal solution of the silicate of a potassium silicate or a specific silicate is added to an ammonium hydroxide solvent. After adding a fluorescent substance 4, the mixture obtained as a result is stirred powerfully. While filtering and taking out the fluorescent substance 4 which has coating, it dries at 100 degrees C.
[0034] It is advantageous to coating that SiO2 is included [in a predetermined case] in addition to silicate. In order to manufacture such coating, the colloidal solution of a borosilicate, a phospho silicate, or an alkali silicate is added to an ammonium hydroxide solution. After adding a fluorescent substance 4, the solution of the tetraethyl orthosilicic acid salt in ethanol (tetraethyl orthosilicate) is added to mixture, and the mixture obtained as a result is stirred powerfully. The fluorescent substance 4 which has coating is dried at 100 degrees C while it is taken out.
[0035] In order to increase stability, the 2nd coating layer can be prepared. For this reason, as already explained, the colloidal solution of a borosilicate, a phospho silicate, or an alkali silicate is added to an ammonium hydroxide solution. First, the fluorescent substance 4 which already prepared coating is added to this mixture, and the solution of the tetraethyl orthosilicic acid salt in ethanol (tetraethyl orthosilicate) is added after that. After stirring powerfully, while taking out the fluorescent substance 4 which carried out duplex coating, it dries at 100 degrees C.
[0036] In order to form coating of an inorganic material, suspension including the combination of a desired coating ingredient, for example, oxide, a borate, phosphate, or these coatings ingredient is made.
[0037] It is converted into instead of by the desired particle by heat treatment after that also including the precursor of the coating ingredient according [suspension] to this invention. First, the suspension which follows, for example, contains Mg (OH)2 is prepared on the particle of a fluorescent substance 4, and is thermally converted into the layer of MgO after that.
[0038] Let especially the initiation compound used for coating containing MgO, aluminum2O3, and oxide like SiO2 be a water-soluble metal salt, a water-soluble nitrate, acetate, or citrate. One or more of the metal salts of these are underwater dissolved, while making a coating solution, and a pH value is adjusted to 7. The fluorescent substance 4 which should be covered is diffused in this solution. Thus, the aqueous suspension of the obtained fluorescent substance 4 continues contacting the ambient atmosphere which contains ammonia with scrambling until an oxide or a hydroxide precipitates to a fluorescent substance particle, while the pH value of suspension rises to 9.5. The fluorescent substance 4 which has coating is removed, and it dries. When a fluorescent substance is covered with a hydroxide, it is calcinated at the temperature which rises gradually and is converted into the oxide with which a hydroxide corresponds.

[0039] In order to cover a fluorescent substance 4 with SiO2, it prepares first suitably, the silicic acid anhydride which can be hydrolyzed, for example, the tetraethyl orthosilicic acid, of a monomer. After adding a fluorescent substance 4, the mixture obtained as a result is stirred powerfully, and a solvent, for example, ethanol, is removed after that. The fluorescent substance 4 which has coating is exposed to the ambient atmosphere saturated with a 80-degree C steam in order to obtain coating of SiO2 of high density.
[0040] The silicic acid anhydride which can be hydrolyzed may beforehand already be condensed selectively. For this reason, it mixes in the amount of catalysts of Rarefaction HCl, and the silicic acid anhydride of a monomer is heated under reflux for 24 hours. Then, distillation removes, without including the silicic acid anhydride beforehand condensed in the solvent.
[0041] Let the initiation compound used to coating containing an orthophosphate be the fusibility metal salt which has presentation MX3 and H2O. In this case, M expresses one of Metals aluminum, Sc, Y, Lu, and La, X expresses one or more of anion CH3COO-, RO-, NO3-, Cl-, CH3COCH=C(O-) CH3, and -OOCCH2CH(OH) (COO-) CH2COO-, and y expresses the number more than zero. Generally as a solvent, water is used.
[0042] a phosphoric acid -- a phosphoric acid and a urea are suitably added to this solution 85%. After filtering suitably the solution obtained as a result with a thin film nylon filter, a fluorescent substance 4 is added. It heats stirring suspension until the pH value is set to 7. After cooling to a room temperature, the fluorescent substance 4 which has coating 4 is taken out, rinsed and dried.
[0043] In order to form coating constituted from a polyphosphate, the water solution of a polyphosphate is added to the suspension of the fluorescent substance 4 which should be covered. A polyphosphate has presentation (M0.5PO3) n, and chooses M from the group of calcium, Sr, and Ba in this case, and chain length n is between 101 and 106. The water solution of the water-soluble salt of calcium, Sr, or Ba is added to this suspension. The pH value of suspension is held to an alkali field by adding ammonia or the caustic alkali solution of sodium. The fluorescent substance 4 which has coating is taken out, rinsed and dried.
[0044] In order to form coating constituted from way acid chloride, the suspension of the fluorescent substance 4 which should be covered is added to the alcoholic solution of way acid ester, and the ester is obtained from the multi-way acid (polyboric acid) which has general formula Hn-2BnO2n-1. In this case, it is n<=3. The reaction mixture obtained as a result is stirred at a room temperature for 2 to 24 hours, and the fluorescent substance 4 which has coating is taken out, and it is dried.
[0045] The example of this invention is explained to a detail below.
[0046] an example 1 -- first -- 30.0g (TEOS) of tetraethyl orthosilicic acid salts in 40.0ml dehydrated ethanol -- 0.1M It mixes to HCl0.864ml. The reaction mixture obtained as a result is heated under reflux for 24 hours. Then, TEOS and ethanol to which condensation was not performed are removed by distillation.
[0047] SrS:Eu10g is suspended in 50.0ml of dehydrated ethanol. TEOS condensed beforehand is added to this suspension, and the mixture obtained as a result is stirred for 15 minutes. SrS:Eu which covered TEOS obtained as a result after distillation of the solvent in a vacuum is exposed to the air containing a steam with a temperature of 80 degrees C. Thickness of coating of SiO2 is set to 100nm.
[0048] A table 1 shows that quantum efficiency hardly decreases by coating of the fluorescent substance particle of SrS:Eu by the layer of SiO2 which has 100nm thickness.
[0049] Table 1: Quantum efficiency (Q. E.) of SrS:Eu which covered SiO2, and SrS:Eu, absorption (Abs.), and surface presentation [table 1]

	QE [%]	Abs. [%]	Sr [原子%]	S [原子%]	O [原子%]	Si [原子%]	C [原子%]
SrS:Eu	100	76.4	16.3	14.2	66.3	-	3.2
SiO_2-SrS:Eu	97	77.6	-	-	46.3	12.5	41.2

[0050] Next, the light emitting device 1 which has the fluorescence layer 2 containing SrS:Eu which covered the diode 3 which emits blue glow, and SiO2 is manufactured. For this reason, the InGaN/AlGaN diode 3 is surrounded by the clear layer 5 of polyacrylate. A clear layer 5 contains further SrS:Eu which covered SiO2 as a fluorescent substance 4. Then, a light emitting device 1 is protected by the epoxy housing 6.
[0051] Example 2 ammonia 250g is mixed in 750g of water, and 25g of potassium-silicate solutions of colloid (15 % of the weight) is added to this mixture. Then, SrS:Eu is added and the suspension obtained as a result is stirred powerfully. The solution of 10ml of tetraethyl orthosilicic acid salts of ethanol 750ml Naka is dropped at suspension for the period for less than 15 minutes. The reaction mixture obtained as a result is stirred for 90 minutes at a room temperature. Covered SrS:Eu is taken out and it dries at 100 degrees C. The covered

fluorescent substance is again suspended in the mixture of 25g of potassium silicates on ammonia 250g in 750g of water, and colloid. 11. of ethanol, and ethanol 500ml -- 10ml [of inner tetraethyl orthosilicic acid] mixture is dropped at this suspension. The reaction mixture obtained as a result is stirred for 60 minutes at a room temperature. SrS:Eu which has coating of a potassium silicate is taken out and it dries at 100 degrees C.
[0052] Subsequently, the light emitting device 1 which has the fluorescence layer 2 containing SrS:Eu which covered the diode 3 and the potassium silicate which emit blue glow is manufactured. For this reason, the InGaN/AlGaN diode 3 is surrounded by the clear layer 5 of polyacrylate. If a fluorescent substance 4 is formed on a clear layer 5, the fluorescence layer 2 containing SrS:Eu which covered the potassium silicate will be formed. Then, a light emitting device 1 is protected by the epoxy housing 6.
[0053] Example 3aluminum(NO3)3.9H2O4.45g is dissolved into 1.25l. of pure water. 85%H3PO41.37g and 36.04g of ureas are added to this solution. SrGa2 S4 is added after filtering the mixture obtained as a result in the nylon filter of 0.2 micrometers of thickness. Suspension is stirred at 90 degrees C until the pH value of a solution is set to 7. Suspension can be cooled to a room temperature, and ejection and pure water wash fluorescent substance SrGa2 S4 which covered AlPO4 several times, and it heats at 100 degrees C for 1 hour.
[0054] Subsequently, the light emitting device 1 which has the fluorescence layer 2 containing SrGa 2O4 which covered the diode 3 and AlPO4 which emit blue glow is manufactured. For this reason, the InGaN/AlGaN diode 3 is surrounded by the clear layer 5 of polyacrylate. A clear layer 5 contains further SrGa2 S4 which covered AlPO4 as a fluorescent substance 4. Then, a light emitting device 1 is protected by the epoxy housing 6.
[0055] Example 4(3.9 mols) Mg(NO3)2.6H2O1.0g is dissolved into 50ml of water. Y3aluminum 5O12 is suspended in 50ml of water, and a magnesium nitride solution is added to this suspension. The suspension which has the pH value of 7.5 and which was obtained as a result is stirred powerfully. The pH value of suspension rises to pH9.1 with concentration ammonia liquor, consequently Mg (OH)2 begins to precipitate. After stirring powerfully for 2 hours, the fluorescent substance with which coating was performed is taken out, and it dries at 80 degrees C, and is eventually calcinated at 250 degrees C for 2 hours.
[0056] The light emitting device 1 which has the fluorescence layer 2 containing Y3aluminum 5O12 which covered the diode 3 which emits blue glow, and MgO is manufactured. For this reason, for this reason, the InGaN/AlGaN diode 3 is surrounded by the clear layer 5 of polyacrylate. A clear layer 5 contains further Y3aluminum 5O12 which covered MgO as a fluorescent substance 4. Then, a light emitting device 1 is protected by the epoxy housing 6.

[Translation done.]